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RESS REPORT

FIFTH QUARTER

JULY - SEPTEMBER 1964

DEVELOPMENT OF THIN ORGANIC ROLLED FILM CAPACITOR

UNION CARBIDE

UNION CARBIDE CORPORATION

LINDE DIVISION

KEMET DEPARTMENT

RESEARCH AND DEVELOPMENT WORK ON DEVELOPMENT

OF THIN ORGANIC ROLLED FILM CAPACITOR

BUREAU OF SHIPS CONTRACT NObsr-89519

FIFTH QUARTERLY PROGRESS REPORT

JULY 1, 1964 - SEPTEMBER 30, 1964

DEVELOPMENT OF THIN ORGANIC

ROLLED FILM CAPACITOR

BUREAU OF SHIPS CODE 606/681A2

SUBJECT

Bureau of Ships Contract NObsr-89519
Quarterly Research and Development Report,
July 1, 1964 - September 30, 1964

REFERENCE

Project Serial No. SR0080302 ST 9636

PROGRAM OBJECTIVES

To develop a capacitor, using ML-1 film as the dielectric, capable of 100 volt operation over the temperature range of -55 to 170 °C, which is twenty times smaller than equivalent CQ05 per MIL Specification MIL-C-19978B. Such capacitor to exhibit dissipation of .01%; insulation resistance of at least 15 ohm farads at 170 °C; temperature coefficient of less than 250 ppm/°C; 250% dielectric withstanding voltage; no capacitance shift with frequency; less than 5% change in capacitance after life test.

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TABLE OF CONTENTS

TABLE OF CONTENTS

(Continued)

1. Foils

1.1 Substrate Preparation

Recent work which involved various substrate materials has emphasized the importance of the condition of the surface upon which the dielectric material is deposited. Surface texture as well as surface chemistry appear to have decided effects upon the stress level at which the deposited dielectric may be operated.

The data indicate that the preferred substrate has a very fine texture surface not contaminated with microscopic traces of unstable materials or with macroscopic particles of either stable or unstable materials, i.e., stable over the environmental conditions involved.

The bulk of the aluminum foil used during the life of this contract has not been the ultimate in either smoothness or cleanliness. Improvement of the foil quality was to be pursued by assessing the value of three techniques:

a. Surface Decontamination
b. Mechanical Smoothing
c. Electropolishing

1.2 Surface Decontamination

In the past we have only assumed that the as-supplied aluminum foil surface was partially contaminated with unextracted rolling lubricants and with particulate materials captured during doubling, undoubling, and slitting. The degree of contamination was an unknown, as was its effect on the electrical parameters of the deposited dielectric. In light of the work which was alluded to in Section 1.1, a more intensive examination of the surface of aluminum foil and the methods used in foil manufacture was conducted.

It was noted that practically all of the 0.17 mil foil and an appreciable portion of the 0.25 mil material is pinholed. The pinhole population varies from near zero to hundreds per running foot. It was also observed that occasionally foil would have brownish-yellow stains. It is probable that lower levels of staining occur constantly but pass undetected.

Examination of a sample of foil rolling lubricant indicated that a polymerizable product can be formed when it is heated to 500°C. This contamination acts as a foil-to-foil adhesive and also is responsible for brown stains on the foil. It is likely that unrolling a foil with adjacent layers cemented together at many points produces the observed pinholes.

The rolling lubricant was noted to contain unidentified particulate material ranging in size from 1 μ to 23 μ in cross section. Although the particles are small, they are an appreciable fraction of the foil thickness and could emboss and locally weaken the foil in pinpoint areas.

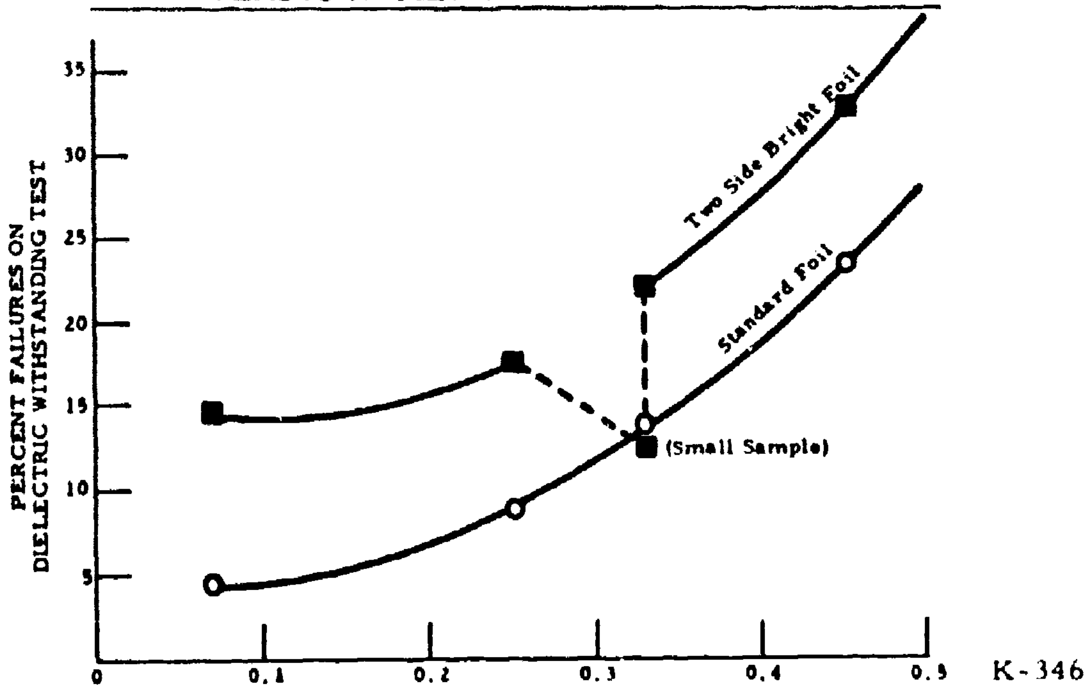
Working with the foil vendor in an effort to correct these deficiencies in the foil has been initiated. Some preventive measures can be taken immediately, but the ultimate solution is dependent on the complete description of the problem and the design of remedial foil manufacturing processes.

1.3 Mechanical Smoothing

Standard aluminum foil is bright one side - matte the other side. Bright both sides foil is available and was described in the Third and Fourth Quarterly Reports. Batches of capacitors of various microfarad values have been prepared and tested in an attempt to ascertain the benefits of using this material. The results reported thus far indicated that no improvement was realized by using both sides bright foil. As further data accumulate this conclusion is substantiated. Figure 1 shows the variation of percent losses at dielectric withstanding voltage test with nominal capacitance for standard foil batches and for both sides bright batches. It is quite apparent that, in this case, both sides bright foil yields inferior devices.

FIGURE 1

DIELECTRIC WITHSTANDING VOLTAGE FAILURES VERSUS NOMINAL CAPACITANCE



Similarly, a comparison of failure rates after 1000 hours for 0.25 µf devices (life tested at 88 volts, 125°C) shows that those made of both sides bright foil had a failure rate 33% higher than those of standard foil.

These conclusions, combined with the observation that the average breakdown voltages on coated foils, as determined by our standard QC test, show only a random dependence on the bright-matte characteristic, indicate that both sides bright foil yields no improvement over the standard foil. It is possible that the benefit expected due to the finer texture is negated by entrapment of rolling lubricant as discussed in Section 1.2. Irrespective of the mechanism, developmental efforts involving both sides bright material will be curtailed pending further technological advances.

1.4 Electropolishing

It has not been possible to generate good electropolished material in large enough quantities to fabricate batches of capacitors. Further work in this area will be suspended in order to devote attention to the more promising area of surface contamination.

2. Coated Foils

2.1 Foil Evaluation

Past work involving metallized ML-1 capacitors has cleared any reservations as to the accuracy of our film thickness measurements (see Appendix to Second Quarterly Report). Calculated and measured capacitances agree to within ±5% which is only slightly more than the calculated error which allows for dimensional errors, mercury load, etc.

The problem of poor correlation between foil breakdown voltage, as described by the QC measurements, and the device dielectric withstanding voltage still persists. Several possible explanations have been offered and investigated; however, no reliable model has been developed nor has any effective corrective measure been found.

Electron micrographs have been made of the film's external surface using a replica. The replica then was stripped, shadowed from 30° and then covered with a backing film. The replicating material was dissolved and the backing film with the shadowed areas was viewed with a transmitted electron beam. Mangifications of 15,000X, 30,000X and 90,000X are shown (see Figures 2, 3, 4 and 5). The dark areas on these pictures are the shadows.

FIGURE 2

ELECTRON MICROGRAPH
ML-1 FILM
15,000X
BRIGHT SIDE

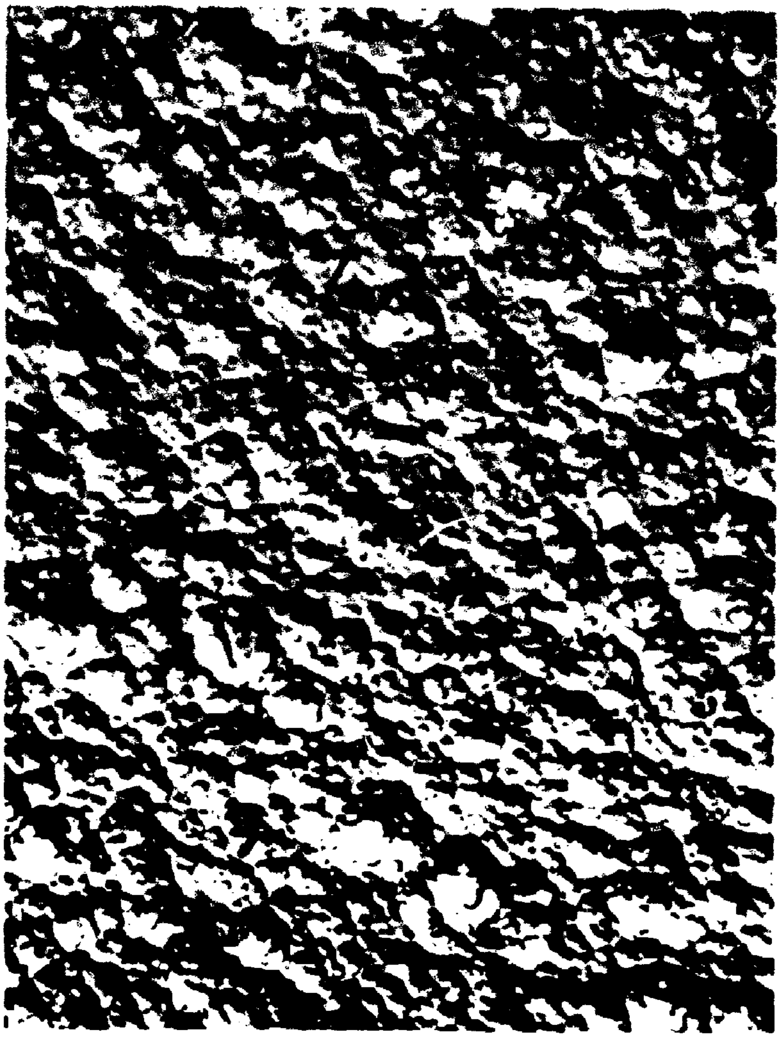


FIGURE 3

ELECTRON MICROGRAPH
ML-1 FILM
30,000X
BRIGHT SIDE

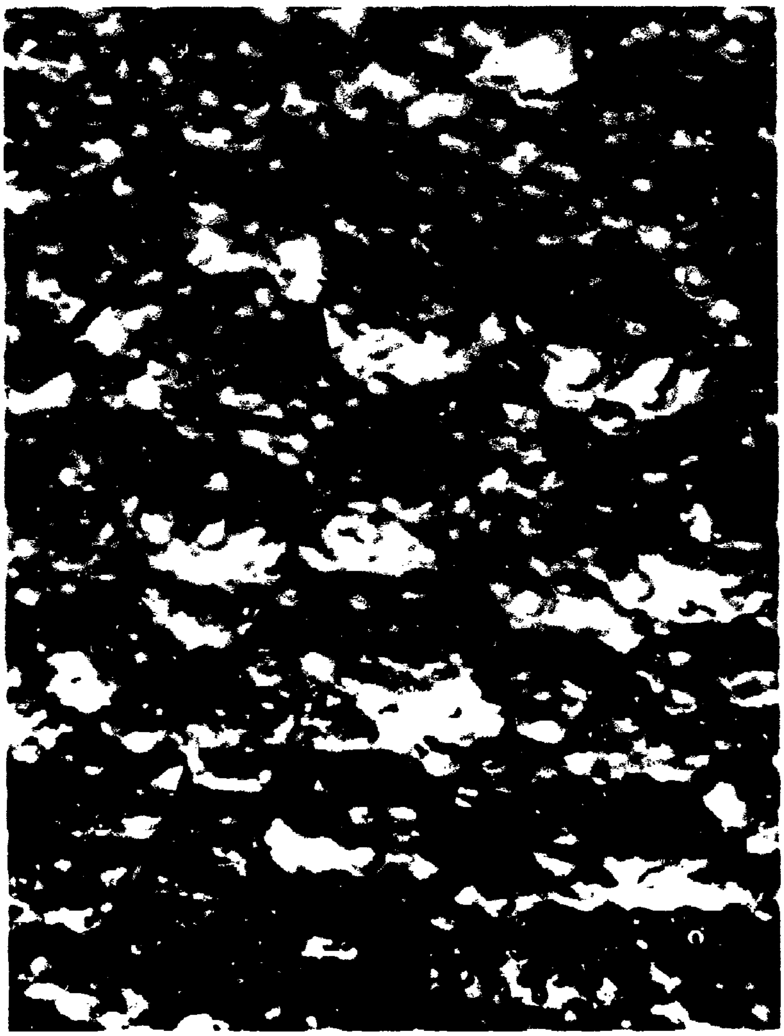


FIGURE 4

ELECTRON MICROGRAPH
ML-1 FILM
30,000X
MATTE SIDE

FIGURE 5

ELECTRON MICROGRAPH
ML-1 FILM
90,000X
BRIGHT SIDE

The major surface irregularities are approximately 1 μ in diameter and 0.2 to 0.3 μ deep. The surface of the bright side film is made up of craters of 1 μ diameter with smaller craters and lumps in them. The matte side film at 30,000X appears to have only major surface variations of 1 μ in diameter by 0.2 to 0.3 μ deep.

It is hoped that these data, upon further analysis, will help us to delineate the mechanism causing our breakdown voltage discrepancies. Further work in this area is warranted. Also, the effect which coated foil history and wave shape of breakdown voltage, using the Microdot instrument, have on the breakdown voltage must be defined.

3. Slitting

3.1 New Slitting Machine

All of the steel parts of the slitting machine have been electrolyzed to prevent oxidation. The machine has been moved to an ultraclean area in which the air-borne contamination reputedly has been reduced to < 100 particles per cubic foot in excess of 1 μ in diameter.

As a result of the utilization of 0.17 mil aluminum foil and of improved operator technique, the slitting process can now be affected much faster and in a more versatile manner than was possible with the 0.25 mil material.

There is a slight tendency for edge beading on the take-up spool. A lay-on roll required to correct this situation is being designed and will be installed when available.

4. Process

4.1 Standard Process Changes

The standard process of ML-1 film capacitors has been changed slightly since the last Progress Report. Prestress, regrind and filling have been eliminated.

Prestress, as discussed in Section 5.1 of the Third Quarterly Report, was a necessity for the elimination of weak or defective parts prior to assembly in cans. Higher quality coated foil and better winding techniques have made prestress superfluous. The regrind operation was used to remove oxidation on the capacitor ends created by prestressing which was done in air at an elevated temperature; this is unnecessary with the elimination of the prestress operation.

The filling operation (First Quarterly Report, Section V-B) has been discontinued, based on the results of an experiment to evaluate its usefulness. Electrical parameters were measured prior to and after 1000 hours of life testing and standard shock and vibration tests were performed on parts with and without the rubber filler.

The results showed no significant differences in electrical parameters although somewhat better shock resistance for filled parts. Three of the eight units tested which were not filled survived shock to 10,000 g; failures occurred at 7000, 8000 and 10,000 g. Ten of the 11 filled capacitors survived 10,000 g shock; the only failure occurred at 10,000 g. All capacitors tested qualified for the medium shock test outlined in MIL-STD-202B, Method 205C. The filled parts qualified for the high impact shock test according to MIL-STD-202C, Method 207A (see Appendix for data).

The processes for ML-1 film capacitors are now performed according to the revised Flow Chart in Figure 6.

4.2 Winding Tension

The rolling tension on the winding machine was adjusted such that half of a group of capacitors were rolled at 500 g and the other half at 250 g. Electrical parameters were measured before and after life testing.

A comparative analysis of the results indicated no significant differences in the electrical characteristics; however, the capacitors wound under 500 g tension had a capacitance shift of -0.15% after 1000 hours of life test (125 °C, 88 volts) while the capacitors wound under 250 g tension had a shift of +1.0%. This indicates that a tighter roll undergoes less physical change and related capacitance shift under life test conditions.

Experimentation is still proceeding in this area since high tension can cause problems during winding and a happy medium must be reached.

4.3 Termination

The new lead wire attachment technique (Fourth Quarterly Report, Section 6.1) for reduced heat input has proved inadequate on the smaller size capacitors. The thermal stresses created by temperature cycling during conditioning have caused the lead wires to come off, resulting in open circuited

ML-1 PROCESS

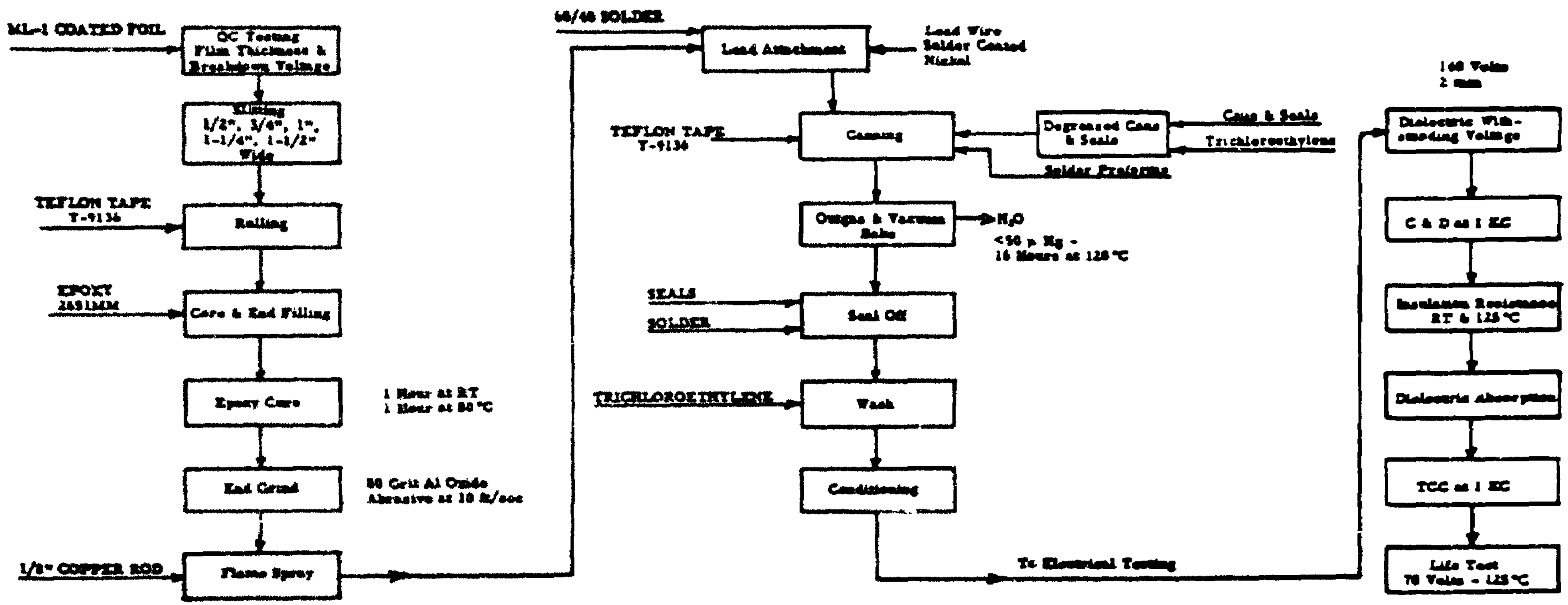


FIGURE 6

capacitors. This problem does not occur in the larger capacitors since the end surfaces offer more area for a stronger solder bond.

Recent measurements have indicated that a reduced heat input is not necessary for the smaller capacitors (0.01 and 0.02 µf). The dissipation is inherently so low that the increase caused by the heat does not cause the dissipation to exceed 0.01%.

Based on these results, it may be necessary to use two different methods of termination, dependent upon the physical size of the capacitor. Future experiments have been proposed to explore this conclusion.

4.4 Can Atmospheres

The capacitors back-filled and sealed in various atmospheres, as described in the Third Quarterly Report, Section 5.3, have finished 1000 hours of life testing. The pertinent data are listed below:

Variable	Average ΔC - %	Average DF_0 - %	Average DF_{1000} - %	IR_0 Megohms	IR_{1000} Megohms	Failure Rate %/1000 Hours
Air	1.70	0.024	0.028	4.5×10^3	7.6×10^2	13
Argon	2.80	0.020	0.024	3.3×10^3	1.4×10^3	17
SF_6-N_2	0.98	0.019	0.027	7.3×10^3	4.2×10^3	0

Subscripts - $_0$ - Before Life Test

$_{1000}$ - After Life Test

ΔC - Capacitance Change After 1000 Hours

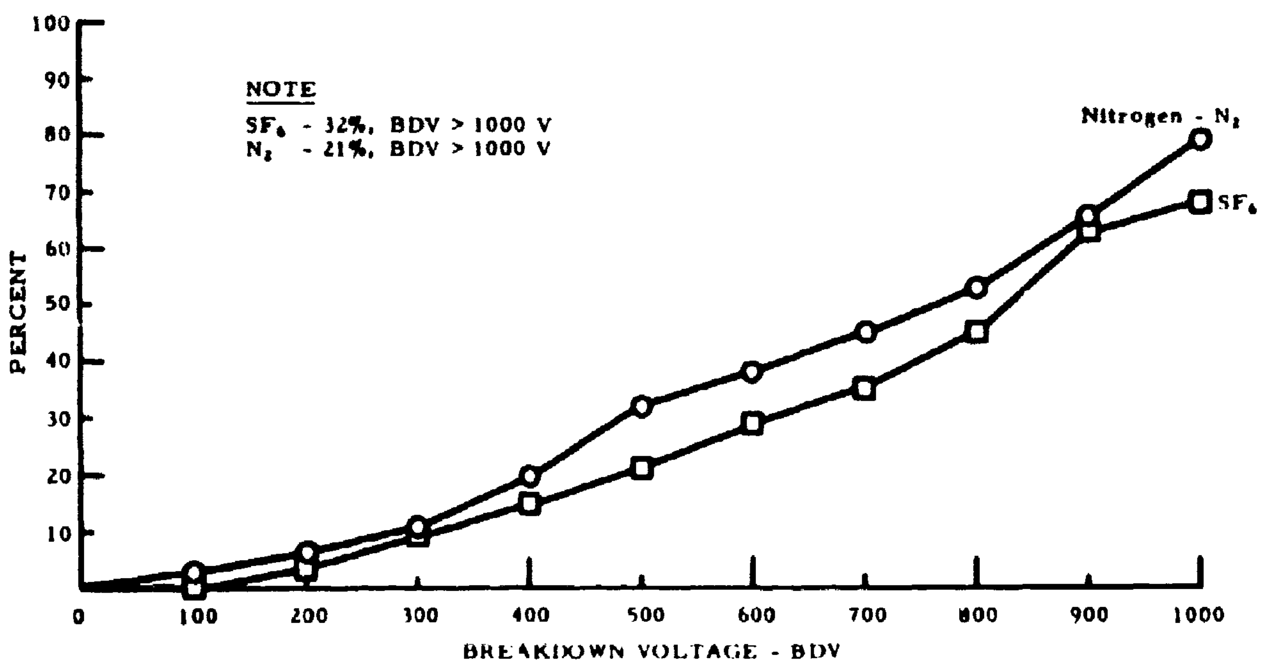
The average insulation resistance of the capacitors sealed in air decreased to an intolerable value, whereas the averages of the capacitors sealed in argon and SF_6 decreased only slightly. The decrease in insulation resistance while under life test is not uncommon; however, the change which occurred in the capacitors sealed in air is extreme.

The capacitors sealed in argon had the highest failure rate and capacitance shift, whereas the capacitors sealed in SF_6 had a zero failure rate and a minimum capacitance shift. It has been postulated that the reason for the high failure rate is due to a corona discharge in the gas. This discharge could occur because of the high electric field created by the proximity of the electrodes. If a dielectric gas with electron attachment capabilities is introduced between the electrodes, the electrons would be captured and discharge would not be possible. SF_6 has good electron attachment capabilities, air has less, and nitrogen and argon cannot attach electrons. The resultant life test failure rates show a definite relationship of failures to gas used. The information obtained indicates that argon should not be used as a sealing atmosphere and possibly SF_6-N_2 might improve the characteristics. Further experiments are now under way to verify these results.

An experiment was performed to establish the BDV characteristics of capacitors sealed in N_2 and SF_6. Eighty-seven ML-1 capacitors, 0.02 μf, were sealed in N_2 and another 87 pieces were sealed in SF_6. These parts were subjected to DC voltages up to 1000 volts. The results indicated that 32% of the parts sealed in SF_6 have BDV's in excess of 1000 VDC, while 21% of the parts sealed in N_2 have BDV's in excess of 1000 VDC. The lowest BDV occurred at 80 volts for N_2 and 150 volts for SF_6. Average BDV's were 680 volts for N_2 and 820 volts for SF_6. These averages assume that 1000 volt survivors fail at 1001 volts; hence, the values are conservative by some unknown measure (see Figure 7).

FIGURE 7

CUMULATIVE PERCENT FAILURES VERSUS BREAKDOWN VOLTAGE



4.5 Conditioning

To facilitate conditioning and to obviate harmful side effects, such as termination failures, conditioning experiments were performed to capacitors at different stages of construction (see Fourth Quarterly Report, Section 7).

A large batch of capacitors was split into four equal groups which were treated in the following manner:

Group 1 - Hot wire termination, conditioned with one ferrule open in vacuum.

Group 2 - Standard termination, conditioned with one ferrule open in vacuum.

Group 3 - Conditioned as flame sprayed rolls (no lead wires) in vacuum.

Group 4 - Conditioned as finished parts.

Measurements showed Group 4 parts had better retrace (Figures 8, 9, 10, 11); Group 3 parts had higher TCC, otherwise there were no significant differences in electrical characteristics.

FIGURE 8

TYPICAL DYNAMIC TEMPERATURE COEFFICIENT AND RETRACE

GROUP I

Hot Wire Termination
Conditioned With One Ferrule Open

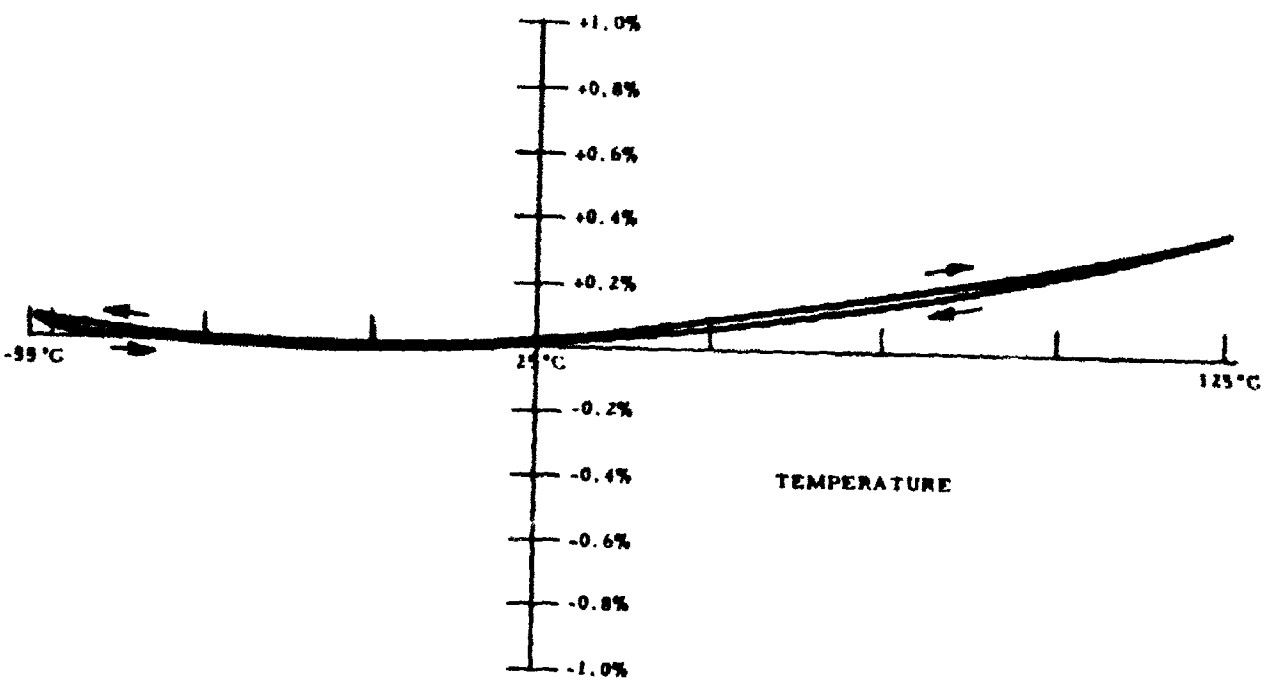


FIGURE 9

TYPICAL DYNAMIC TEMPERATURE COEFFICIENT AND RETRACE

GROUP 2

Standard Termination
Conditioned With One Ferrule Open

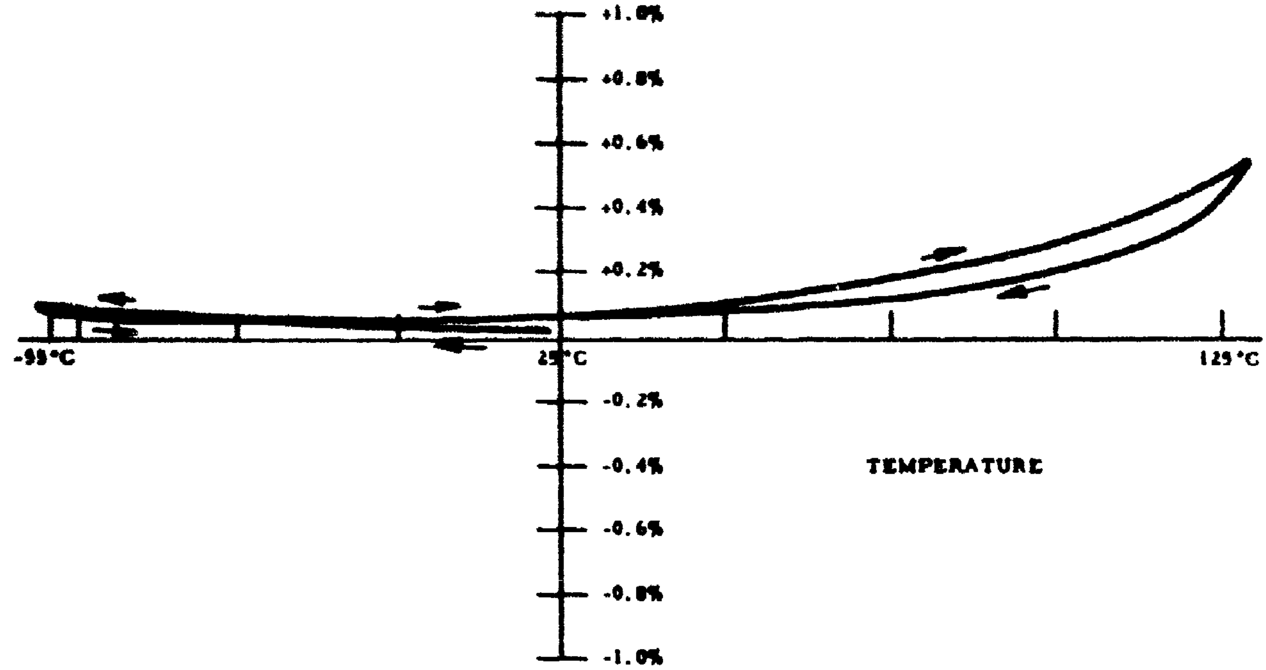


FIGURE 10

TYPICAL DYNAMIC TEMPERATURE COEFFICIENT AND RETRACE

GROUP 3

Conditioned in Flame Sprayed Roll

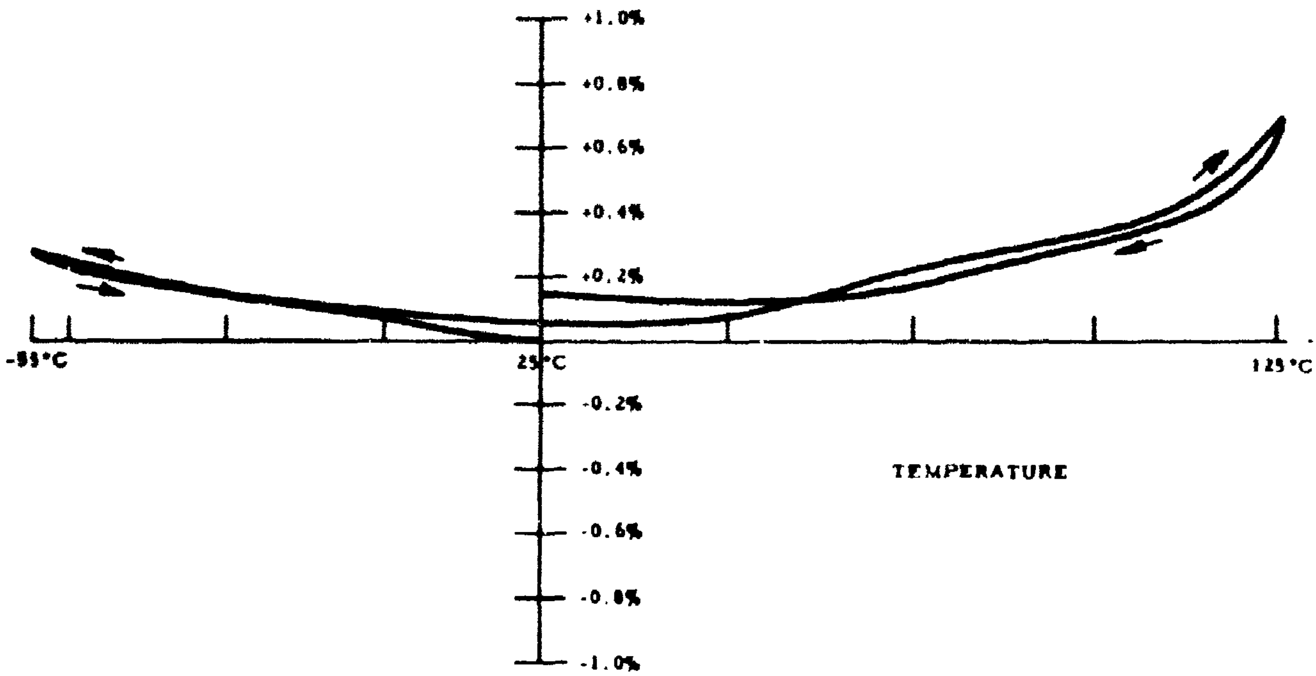
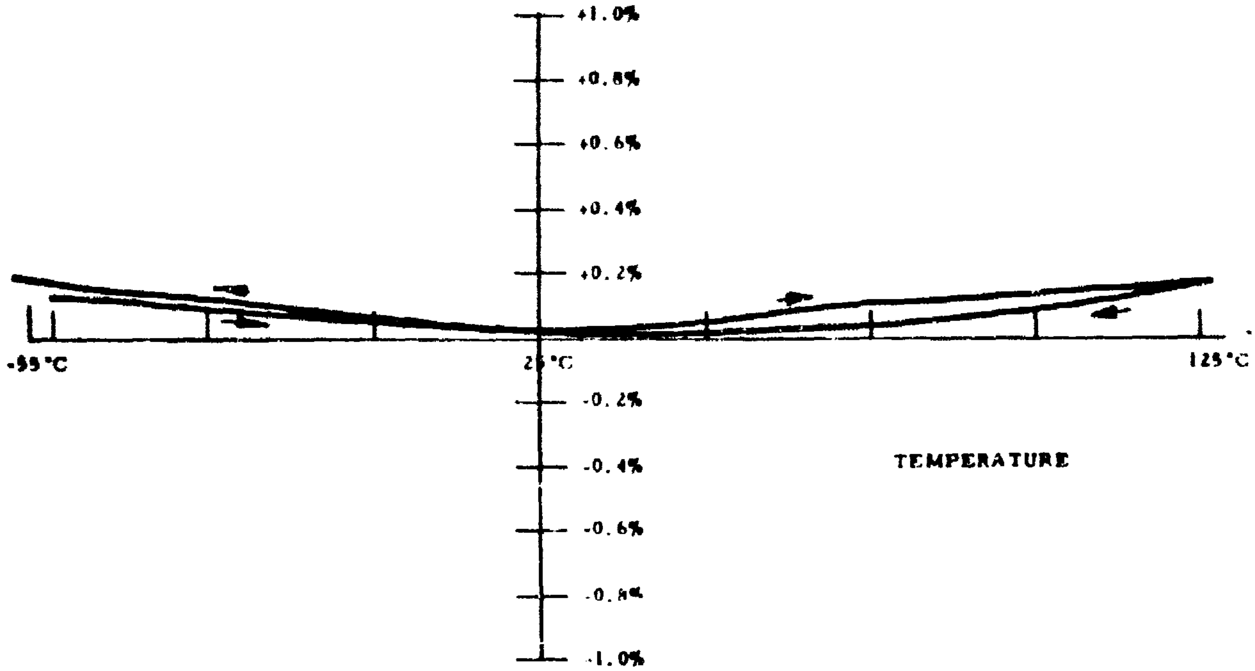


FIGURE 11

TYPICAL DYNAMIC TEMPERATURE COEFFICIENT AND RETRACE

GROUP 4

Conditioned as Sealed Parts



5. Metallized Type ML-1 Film Capacitors

5.1 Tab Terminated Devices

The group of 20 capacitors (designated batch DW) introduced in Section 4.2.1 of the Fourth Quarterly Report have completed 1500 hours of life test at 70 VDC and 125°C. There were no failures on life test. A summary of the electrical test data on this batch is given in Table I.

TABLE I

BATCH DW ELECTRICAL TEST DATA

Test Period	Capacitance µf	DF at 1 kc %	IR 125°C Megohms	TCC ppm/°C	ΔC During TCC	DA - %
Before Life Test	0.2594	0.120	4.2×10^3	- 55, -199 + 85, -248 +125, -275	±0.02%	0.077
After 500 Hr Life Test	0.2605	0.183	3.7×10^3	- 55, -139 + 85, -251 +125, -280	-0.21	0.378
After 1500 Hr Life Test	0.2649	0.146	1.4×10^4	- 55, -176 + 85, -213 +125, -288	-0.11	0.500

Five of the devices were tested for breakdown voltage. The capacitors were placed directly across a DC potential and the potential was raised from zero at a rate of 40 volts per second. Breakdown was defined as that condition at which the steady state DC current was in excess of 10 ma. These data are shown in Table II. Upon disassembly of these units it was found that failure had occurred around the periphery of the tab in all cases.

TABLE II

BATCH DW DESTRUCTIVE BDV TEST

Cap. No.	Breakdown Voltage VDC
DW-23	180
DW-24	230
DW-20	240
DW-21	200
DW-18	220

A softer and smoother tab must be devised before this type of capacitor can be produced successfully. Under current conditions the full potential of the dielectric cannot be utilized because of the degradation caused by the tab.

The test results thus far certainly imply that the ML-1 dielectric is compatible with the metallized electrode concept. Other techniques of fabrication must be investigated however, and the exact nature of the self-healing properties of a metallized ML-1 capacitor must be defined.

APPENDIX

ML-1 VIBRATION TEST DATA

Vibration Level: 30 G (60-2000 cps)
Scanning Rate: Logarithmic
Test Duration: 1-1/2 Hours
Capacitor Type: R22/75

Sample No.	Initial Measurements		After Vibration	
	Capacitance	% Dissipation	Capacitance	% Dissipation
		Lot: DP[1]		
11	0.2080	0.035	0.2080	0.040
34	0.2208	0.025	0.2208	0.030
37	0.2052	0.035	0.2053	0.040
42	0.2272	0.030	0.2263	0.035
		Lot: DT[1]		
12	0.2565	0.040	0.2565	0.030
24	0.2195	0.030	0.2193	0.030
30	0.2527	0.025	0.2529	0.033
34	0.2409	0.030	0.2409	0.035

Notes:

1. With silicone rubber fill.
2. Capacitance and DF measurements were made on E.S.I. bridge (Model 277) at 1000 cps with 0 DC bias.

ML-1 SHOCK TEST DATA

Capacitor Type: R22/75

No.	Before Potting Capacitance	Before Potting % D	After Potting Capacitance	After Potting % D	After 10,000 G's Capacitance	After 10,000 G's % D
			Lot: DT[1]			
3	0.2486	0.40	0.2485	0.040	0.2485	0.040
4	0.2574	0.040	0.2573	0.040	0.2573	0.040
6	0.2233	0.035	0.2232	0.035	0.2232	0.035
7	0.2460	0.040	0.2458	0.040	0.2458	0.040
9	0.2367	0.030	0.2366	0.035	0.2366	0.035
14	0.2316	0.040	0.2316	0.040	0.2316	0.040
19	0.2211	0.040	0.2212	0.030	OPEN[7]	
24	0.2190	0.031	0.2190	0.030	0.2190	0.030
27	0.2557	0.040	0.2554	0.040	0.2554	0.040
42	0.2089	0.030	0.2088	0.025	0.2088	0.025
49	0.2453	0.040	0.2454	0.040	0.2454	0.040
			Lot: DP[2]			
15	0.2398	0.045	0.2398	0.045	INTERMITTENT[4]	
20	0.2281	0.035	0.2283	0.030	0.2281	0.035
21	0.2248	0.035	0.2248	0.035	INTERMITTENT[4]	
24	0.2176	0.035	0.2176	0.030	INTERMITTENT[6]	
30	0.2183	0.035	0.2183	0.040	0.2183	0.040
34	0.2053	0.040	0.2050	0.050	0.2053	0.040
37	0.2223	0.040	0.2223	0.035	INTERMITTENT[6]	
41	0.2145	0.035	0.2145	0.050	INTERMITTENT[5]	

Notes:

1. Lot DT - with silicone rubber fill.
2. Lot DP - without silicone rubber fill.
3. Shock was perpendicular to axis of capacitor from 1000-10,000 G's in steps of 1000 G's.
4. Intermittent operation observed after 7000 G, 0.2 MS shock.
5. Intermittent operation observed after 8000 G, 0.2 MS shock.
6. Intermittent operation observed after 9000 G, 0.2 MS shock.
7. Open observed after 10,000 G, 0.2 MS shock.
8. Capacitance and DF measurements were made on E.S.I. (Model 277) bridge at 1000 cps.

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